Report on the synthesis of a lubricant sample (REF SPC 93-4036)

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(This report completes the second agreement)

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The objective of this project was to further develop the techniques associated with the preparation of samples of substituted perfluoropolyethers, including the preparation of a 10 to 20 gram sample of perfluoropolyether for lubricant testing by the USAF.

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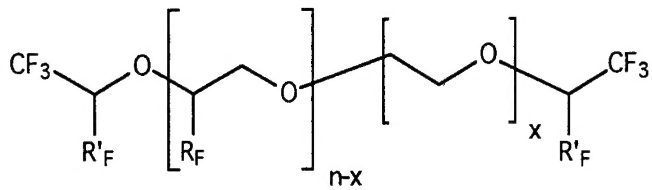
Introduction

The objective of this project was to further develop the techniques associated with the preparation of samples of substituted perfluoropolyethers, including the preparation of a 10 to 20 gram sample of perfluoropolyether (1) for lubricant testing by the USAF.



(1)

(n = ca 22, n-x = ca 13)
(R_F = $CF_3CF_2CF_2$, R'_F = R_F (predom) or F, all unmarked bonds to F)

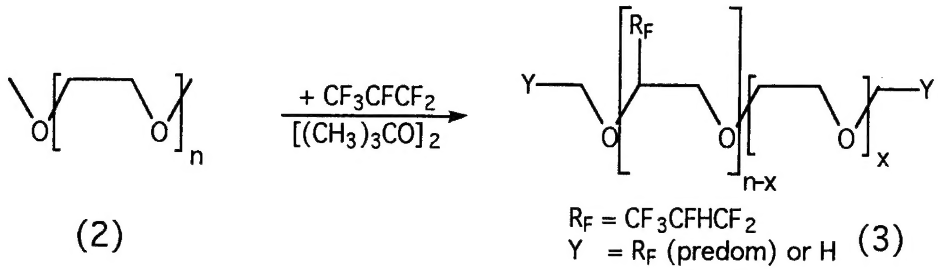
(Note: Chambers, US Patent 4,877,905)

Experimental

a) Starting materials

Dimethylpolyethylene glycol(1000) {n = 22.3} was supplied by Merck-Schuchardt, ditertiarybutylperoxide was supplied by Aldrich Chemical Company Limited. Hexafluoropropene was supplied by Fluorochem Limited. 50% Fluorine/Nitrogen mixture was supplied by Air Products.

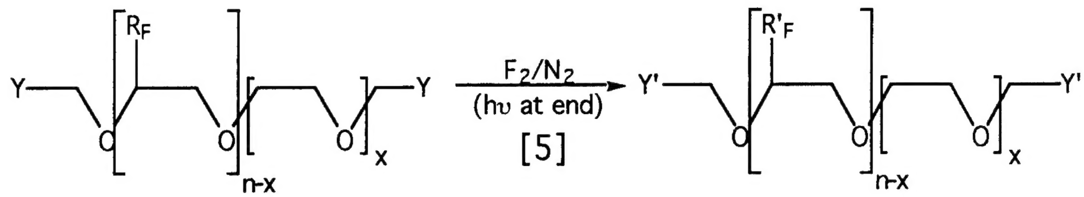
b) Reaction of Dimethylpolyethylene glycol (2) with hexafluoropropene



(2) (3)

Into a 300ml stirred autoclave was introduced (2) (94.0g, 0.91 moles), and ditertiary butyl peroxide (6.3g, 0.043 moles). Dissolved oxygen was removed by introducing high pressure nitrogen gas (15 Bar), stirring, and carefully venting (repeated twice). The autoclave system was then evacuated. Hexafluoropropene gas (*ca* 10g) was introduced and the autoclave was heated to 130°C with stirring. Hexafluoropropene was then allowed to pressurise the autoclave from a room temperature cylinder. The autoclave contents were heated to and then maintained at a temperature of 140°C for *ca* 2 hours until the uptake of hexafluoropropene gas had ceased. This procedure was repeated with fresh initiator four times, taking samples each time. Finally a portion of product with fresh initiator (6.7g) was reacted further with hexafluoropropene. The autoclave contents were heated to 140°C during which time the internal pressure rose to *ca* 20 Bar. After stirring for a period of 2.5 hours the autoclave was cooled and opened. N.M.R. analysis of the stripped product (an orange oil) (3) indicated that there were *ca* 15.5 hexafluoropropyl groups per polyethylene glycol molecule.

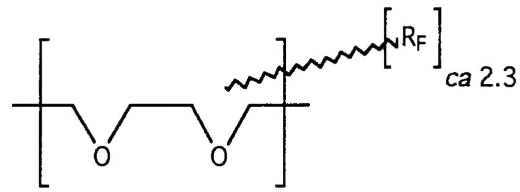
c) Reaction of (3) with fluorine/nitrogen mixtures



(3) (all unmarked bonds to hydrogen)

$R_F = CF_3CFHCF_2$
$Y = R_F$ (predom) or H
$R'_F = CF_3CF_2CF_2$
$Y' = R'_F$ (predom) or F
n-x *ca* 13.5, n *ca* 22

(1) (all unmarked bonds to fluorine)



(4) (all unmarked bonds to hydrogen)

A solution of (3) (21.3g) in (4) (99.9g) was introduced into a stirred FEP reaction vessel. A F_2/N_2 mixture containing initially 5% F_2 rising to 50% F_2, was passed into the vessel at room temperature. When the reactivity had decreased the mixture was transferred into an FEP tube through which 50% F_2/N_2 was bubbled. At this time *ca* 59% of the hydrogen atoms had been replaced by fluorine. Perfluorination was effected by passing 50% F_2/N_2 through the mixture under ultra violet irradiation (100W then 1000W). The volatile, now perfluorinated, solvent (85g) was removed under reduced pressure (150°C, <1mmHg) leaving a colourless viscous oil (16g) (1). A small quantity of higher molecular weight solid polyether was also obtained (*ca* 0.7g). Many n.m.r. samples were removed during fluorination to monitor the process, hence, the weight of the final product does not reflect the efficiency of the process. A sample of (1) (12.0g) was sealed into two evacuated ampoules (2 of 6g) and dispatched to A. Davison, Euro. Off. Aerospace R+D (AFSC), 223/231 Old Marylebone Road, London NW1 5TH for forwarding to Wayne Ward at Wright Patterson AFB, Ohio.

Characterisation of Intermediates/Products

Estimation of degree of hexafluoropropene incorporation

To an n.m.r. sample ($CDCl_3$ as solvent) was added 1 to 4 drops of α,α,α-trifluorotoluene. By determining the ratio of high field ^{1}H & ^{19}F n.m.r. integrals of the sample and trifluorotoluene it was possible to assess the extent of hexafluoropropene incorporation.

Estimation of degree of fluorination

To an n.m.r. sample ($CDCl_3$ as solvent in early stages of fluorination, neat in later stages) was added 1 to 4 drops of α,α,α-trifluorotoluene. By determining the ratio of high field ^{1}H & ^{19}F n.m.r. integrals of the sample and trifluorotoluene it was possible to assess the extent of fluorination knowing the extent of hexafluoropropene incorporation.

^{19}F N.M.R. of (1)

See Appendix 1 for 235MHz n.m.r. spectrum.

^{13}C N.M.R of (1)

At 62.9MHz multiple overlapping resonances between100 and 125 ppm.

Elemental Analysis of (1)

Elemental analysis indicated 0.0% Hydrogen and 22.7% Carbon.

Summary

A perfluorinated polyether of novel structure has been produced. Aspects of the larger scale synthesis of such materials have been developed. We look forward to further development of syntheses of new materials of novel structure, for testing as lubricants in arrangement with Wright Patterson AFB, Ohio, USA.

Appendix 1.

^{19}F NMR of Perfluoropolyether Sample (1)